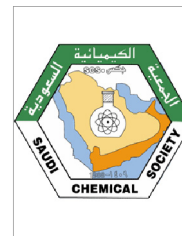




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ORIGINAL ARTICLE

Synthetic, spectroscopic, magnetic and thermal aspects of drug based metal complexes derived from 1st row transition metal ions

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Abstract A newly synthesized ligand, 5-((1*H*-indol-1-yl)methyl)quinolin-8-ol (L) was characterized by ¹H NMR, ¹³C NMR, DEPT-135 and IR spectroscopic techniques. The synthesized metal complexes were characterized using elemental analyses, (infrared, electronic and FAB mass) spectra, magnetic measurements and thermogravimetric analyses. Kinetic parameters such as order of reaction (*n*) and the energy of activation (*E_a*) are reported using the Freeman–Carroll method. The pre-exponential factor (*A*), the activation entropy (ΔS^\ddagger), the activation enthalpy (ΔH^\ddagger) and the free energy of activation (ΔG^\ddagger) were calculated. Metal complexes are also screened for their *in vitro* antibacterial activity against a range of Gram-positive and Gram-negative organisms.

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1. Introduction

In recent decades, the construction of metal–organic coordination architectures has witnessed tremendous growth because of their intriguing structures and potential properties (Kesanli and Lin, 2003; Rosi et al., 2005; Cao et al., 2002; Ye et al., 2005). During recent years, there has been an intense investigation of different classes of indole and their derivatives which are an important group of heterocyclic compounds, and thus

play a fundamental role in organic and bioorganic chemistry. Derivatives of 1*H*-indole possess various pharmacological activity (Patel et al., 2012; Munjal and Gupta, 2010), anti-inflammatory (Zhou et al., 2000), metal binding abilities (Shimazaki et al., 2009) and also act as therapeutic agents (Joule, 2000. In *Science of Synthesis: Houben-Weyl Methods of Molecular Trans – Formations*. Stuttgart, Germany) and breast cancer inhibitory activity (Karthik et al., 2004). 1*H*-indole and its various derivatives have also been used for the preparation of metal complexes based on first row transition metal (Khaleedi et al., 2011). Among the class of hydroxyquinolines, the chemistry of 8-hydroxyquinolines has attracted a special interest due to their diverse biological properties (Chaudhari and Rindhe, 2011; Patel et al., 2012) such as anti-dyslipidemic activity, antioxidative activity (Sashidhara et al., 2009), antiseptic and antiplaque (Burckhalter and Leib, 1961; Dale et al., 1978), antimalarial (Vanparia et al., 2010),

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antituberculous (Kolehmainen et al., 2012), antidiuretic (Ukrainets et al., 2000), anticancer (Madonna et al. 2010; Blunden et al., 1987), antibacterial and antifungal activities (Patel and Patel, 2011; Srisung et al., 2013).

One of derivatives of 8-hydroxyquinoline, 5-chloromethyl-8-quinolinol (CMQ) can be synthesized easily and has been studied extensively (Peng et al., 2007). Thus, looking at the pharmaceutical importance of indole and CMQ, it was decided to synthesize metal complexes using ligand containing both, indole and CMQ. This may afford a compound having not only the metal gripping potentiality but also possibly possess good biological efficiency due to the indole derivative. Hence, the present article describes the synthesis and characterization of novel metal complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions.

2. Experimental

2.1. Materials

The chemicals used for the synthesis purpose were all of analytical grade, such as 1*H*-indole, 8-hydroxyquinoline (purchased from local market), Luria broth and agar-agar (from SRL, India). Metal (II) salts (chloride/nitrate/sulfate) of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were used in their hydrated form. Silica gel F254 thin-layer chromatographic plates of size 20 × 20 cm were purchased from the E. Merck (India) Limited, Mumbai and used for purity evaluation. The organic solvents were purified by the recommended method (Vogel, 1989. *Textbook of Practical Organic Chemistry*, 5th ed. Longman, London).

2.2. Instruments

The contents of carbon, hydrogen and nitrogen were analyzed with a Perkin Elmer (USA) 2400-II CHN analyzer. The metal contents of the metal complexes were analyzed by EDTA titration (Vogel, 1978. *Textbook of Quantitative Inorganic Analysis*, 4th ed. ELBS and Longman, London) after decomposing the organic matter with a mixture of concentrated HClO₄, H₂SO₄ and HNO₃ (1:1.5:2.5). The melting points were checked using a standard open capillary method and are uncorrected. Infra-red spectra (4000–400 cm⁻¹) were recorded on a Nicolet-400D

spectrophotometer using KBr pellets. ¹H, ¹³C NMR and DEPT-135 spectra were recorded on a Bruker Avance 400 FT-NMR instrument using DMSO-d₆ as a solvent. The FAB mass spectrum of the metal complexes was recorded at SAIF, CDRI, Lucknow with a Jeol SX-102/DA-6000 mass spectrometer. The magnetic moments were obtained by Gouy's method using mercury tetrathiocyanato cobaltate (II) as a calibrate ($g = 16.44 \times 10^{-6}$ c.g.s. units at 20 °C). Diamagnetic corrections were made using Pascal's constant. The reflectance spectra of the free ligand (L) and their metal complexes were recorded in the range 1700–350 nm (as MgO disks) on a Beckman DK-2A spectrophotometer. A simultaneous TG/DTG was obtained using a Model 5000/2960 SDT, TA Instruments, USA. The experiments were performed in a N₂ atmosphere at a heating rate of 10 °C min⁻¹ in the temperature range 50–800 °C, using an Al₂O₃ crucible.

2.3. Synthesis of ligand

The ligand was synthesized by the condensation of 1*H*-indole and 5-chloromethyl-8-hydroxyquinoline hydrochloride. CMQ was prepared and used as the starting material for the synthesis of novel ligand (L) by condensing it with 1*H*-indole as reported in the literature method (Peng et al., 2007).

2.3.1. 5-((1*H*-indol-1-yl) methyl) quinolin-8-ol (L)

The mixture of 1*H*-indole (0.234 g, 0.002 mmol) and CMQ (0.428 g, 0.002 mmol) in 1:1 (water:ethanol) solvent system was refluxed with continuous stirring for about 4–6 h. The completion of the reaction was confirmed by TLC. The excess of solvent was distilled off and the residue was poured into ice-cold water to yield a light green product which was filtered and washed with hot water and ethyl acetate and then dried in vacuum desiccators. Yield, 75%; m.p. 183–185 °C. Calc. (%): C, 78.81, H, 5.14, N, 10.21. C₁₈H₁₄N₂O (274.32) (%): Found (%): C, 78.72, H, 5.11, N, 10.17. IR (ν_{\max} , KBr, cm⁻¹): 3401 (O–H), 1703 (C=N), 1360 (C–O); ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 10.84 (1H, s, protons –OH), 8.91 (2H, d, H15, H16), 7.82 (2H, d, H14, H17), 7.12 (2H, d, H6, H5), 7.4 (3H, m, H1, H2, H3), 4.41 (2H, s, protons N–CH₂); ¹³C NMR (100 MHz, DMSO-d₆, δ ppm): 27.90 (C9), 101.43 (C11), 111.90 (C7), 114.13 (C15), 119.09 (C13), 121.32 (C12), 121.41 (C3), 121.84 (C14), 126.91 (C5), 127.47 (C6), 127.86

Table 1 Analytical and physical data of the ligand and its metal complexes.

Sample No.	Compounds	Formula weight (g mol ⁻¹)	Color (Yield %)	Melting point (°C)	Analysis (%) Calcd. (Found)				μ_{eff} (BM)
					C	H	N	M	
1	Ligand (L) C ₁₈ H ₁₄ N ₂ O	274.32	Light Pink(75)	183–185	78.81 (78.72)	5.14 (5.11)	10.21 (10.17)	–	–
2	[Cu(L) ₂ (H ₂ O) ₂] CuC ₃₆ H ₃₀ N ₄ O ₄	646.19	Dark Pink(82)	283–285	66.91 (66.84)	4.68 (4.66)	8.67 (8.63)	9.83 (9.80)	1.82
3	[Ni(L) ₂ (H ₂ O) ₂] NiC ₃₆ H ₃₀ N ₄ O ₄	641.34	Brown (83)	287–289	67.42 (67.31)	4.71 (4.65)	8.74 (8.70)	9.15 (9.11)	4.02
4	[Co(L) ₂ (H ₂ O) ₂] CoC ₃₆ H ₃₀ N ₄ O ₄	641.58	Dark Pink(82)	281–283	67.39 (67.32)	4.72 (4.69)	8.73 (8.71)	8.19 (8.16)	2.86
5	[Mn(L) ₂ (H ₂ O) ₂] MnC ₃₆ H ₃₀ N ₄ O ₄	634.59	Pink(84)	284–286	67.82 (67.74)	4.74 (4.71)	8.79 (8.78)	8.62 (8.58)	5.6
6	[Zn(L) ₂ (H ₂ O) ₂] ZnC ₃₆ H ₃₀ N ₄ O ₄	648.06	Dark Brown(82)	281–283	66.72 (66.63)	4.67 (4.65)	8.65 (8.64)	10.09 (10.07)	D

(C10), 127.97 (C17), 128.32(C4a), 133.71 (C4), 136.87 (C16), 139.16 (C8a), 147.93 (C8), 152.5 (C2); DEPT-135 (100 MHz, DMSO- d_6), δ ppm): 27.90 (C9), 111.01, 111.90, 114.11, 118.76, 119.09, 121.41, 121.84, 123.80, 127.97, 133.72, 147.93.

2.3.2. General procedure for the synthesis of metal complexes

A warm solution of metal (II) salt (2.5 mmol) in 50% aqueous formic acid (2.5 ml) was added drop by drop with continuous stirring to previously a warmed solution of ligand (L) (5 mmol, 2 equiv.) in 20% aqueous formic acid solution (20 ml). With proper adjustment of the pH (6–7) using 50% NH_4OH , the resultant mixture was further digested in a water bath for 4–5 h and centrifuged. The suspended solid metal complexes were allowed to settle and collected by filtration, washed with sufficient quantity of distilled water and then little hot ethanol and acetonitrile and finally dried in vacuum desiccators over anhydrous calcium chloride. The physical data of ligand and metal complexes are reported in Table 1.

2.4. Bio assay

2.4.1. Minimum inhibitory concentration

The minimal inhibitory concentration (MIC) was ascertained using serial tube dilution technique (Pelczar et al., 1979. **Microbiology, 4th ed. Tata McGraw-Hill, New Delhi**) by variation of compound concentration. The antibacterial activity of the control, standard drug (ciprofloxacin), ligand (L) and its metal complexes was screened using different bacterial strains such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Serratia marcescens*. All the compounds were found to be more potent against bacterial strains compared to standard drug.

3. Results and discussion

The reaction of CMQ with indole afforded light pink crystals of the ligand (L) in good yields. The product shows partial solubility in acetone, methanol, ethanol and acetonitrile, while considerably soluble in polar aprotic solvents like dimethyl formamide (DMF), dimethylsulfoxide (DMSO), organic acids and pyridine. All the prepared metal complexes $[\text{M}(\text{II})(\text{L})_2(\text{H}_2\text{O})_2]$ having the characteristic color are stable in air and practically insoluble in water, ethanol, methanol, chloroform and hexane.

3.1. IR spectra

The important infrared spectral bands and their tentative assignments for the synthesized metal complexes were re-

corded using KBr disks and are summarized in Table 2. In the 8-hydroxyquinoline metal complexes of divalent metals, the $\nu(\text{C}=\text{O})$ appeared in the 1117 cm^{-1} region and the position of the band slightly varied with the metal (Charles et al., 1956). The $\nu(\text{C}=\text{O})$, observed in the free oxine molecule at 1092 cm^{-1} , shifted to higher frequencies in all the metal complexes, giving a strong absorption band at $\sim 1156\text{ cm}^{-1}$. This clearly indicates the coordination of 8-hydroxyquinoline in these metal complexes. The broad band at 3401 cm^{-1} observed in the case of ligand was shifted at $\sim 3326\text{ cm}^{-1}$, which was attributed to $\nu(\text{O}=\text{H})$ of coordinated water molecule. In the investigated metal complexes, the bands observed in the region 3318–3337, 1278–1295, 865–875 and $705\text{--}710\text{ cm}^{-1}$ were attributed to –OH stretching, bending, rocking and wagging vibrations respectively, due to the presence of water molecules. The presence of a rocking band indicates the coordination nature of the water molecule (Pansuriya and Patel, 2007). In the far-IR region, two new bands at ~ 502 and $\sim 536\text{ cm}^{-1}$ in the metal complexes were assigned to $\nu(\text{M}=\text{O})$ and $\nu(\text{M}=\text{N})$, respectively. All of these data confirm the fact that the ligand (L) behaves as a bidentate ligand. The IR spectra of ligand and $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ complex are shown in Figs. 5 and 6.

3.2. Diffuse electronic spectral and magnetic properties data

The diffuse electronic spectra of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ exhibited two bands at 26234 cm^{-1} due to charge transfer and a broad band having maxima at 1500 cm^{-1} due to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition (Abuhijleh et al., 1991). The broadening of the signal might be due to the Jahn–Teller distortion. The absorption bands of the diffuse electronic spectra and value of their magnetic moment favor a tetragonally distorted octahedral geometry around Cu(II) ion (Cotton and Wilkinson, 1992. **The Elements of first row transition series. In: Advanced inorganic chemistry, third ed., Wiley, New York; Dixit et al., 2010**). The spectra of $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$ showed weak bands at 16776, 18421 and 23807 cm^{-1} assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$, ${}^4\text{E}_g$ transitions and their magnetic moment values suggest an octahedral geometry for the Mn(II) ion. $[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$ showed three weak absorption bands at 9974, 16013 and 24464 cm^{-1} corresponding to the characteristic transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$. $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$ exhibited three absorption bands at 9828, 15481 and 22107 cm^{-1} , respectively, due to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions. The absorption bands of the diffuse electronic spectra and values of their magnetic moments show an octahedral geometry around Ni(II) and Co(II) ions (Agarwal et al., 2004). As the spectrum of $[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]$ was not well resolved, it was not well interpreted, but its magnetic moment value shows its

Table 2 The characteristic IR bands of metal complexes.

Compounds	$\nu(\text{O}=\text{H})$ (cm^{-1})	$\nu(\text{C}=\text{N})$ (cm^{-1})	$\nu(\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{M}=\text{O})$ (cm^{-1})	$\nu(\text{M}=\text{N})$ (cm^{-1})
Ligand(L) $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$	3401	1703	1360	–	–
$[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ $\text{CuC}_{36}\text{H}_{30}\text{N}_4\text{O}_4$	3326	1706	1358	502	536
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$ $\text{NiC}_{36}\text{H}_{30}\text{N}_4\text{O}_4$	3368	1712	1352	510	508
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$ $\text{CoC}_{36}\text{H}_{30}\text{N}_4\text{O}_4$	3375	1710	1354	517	538
$[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$ $\text{MnC}_{36}\text{H}_{30}\text{N}_4\text{O}_4$	3352	1706	1358	502	518
$[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]$ $\text{ZnC}_{36}\text{H}_{30}\text{N}_4\text{O}_4$	3367	1708	1342	518	514

diamagnetic nature as expected (Cotton and Wilkinson, 1988. In: *Advanced Inorganic Chemistry*, 5th edn., Wiley Interscience, New York). The results of the magnetic moment value (Table 1) were shown to have octahedral geometry for all the metal complexes. Hence, the observed values of magnetic moments and the electronic spectra of metal complexes supported octahedral geometry for all the structures (Patel et al., 2008). The probable structure of the metal complex is given in Fig. 1.

3.3. Thermogravimetric analysis

In first decomposition step, the weight loss during 50–210 °C corresponded to two coordinated water molecules. A loss in weight observed in the second step corresponded to some part of the ligand molecule (L) in the temperature range 185–455 °C. Finally, liberation of the remaining part of the ligand molecule (L) in the temperature range 455–800 °C was observed and the remaining weight was consistent with metal oxide (Sekerci and Yakupoglu, 2004). The thermodynamic activation parameters of the decomposition process of dehydrated metal complexes such as activation entropy (S^*), pre-exponential factor (A), activation enthalpy (H^*) and free energy of activation (G^*) were calculated using reported equations (El-Zaria, 2008). According to the kinetic data obtained from DTG curves, all the metal complexes have a negative entropy and indicate more ordered systems for the studied metal complexes (Modi and Patel, 2008). The energy of activation (E_a) is helpful in assigning the strength of the bonding of ligand moieties with the metal ion. The relatively high E_a value (Table 4) indicates a strong bonding between the metal ion and the ligand (Jani et al., 2010; Parekh et al., 2005). Thermo analytical and thermodynamic data of metal complexes are reported in Tables 3 and 4, respectively. TG/DTG curves of the Cu (II) metal complexes are shown in Fig. 7.

3.4. FAB mass spectra

In the mass spectra of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$, the peak at $m/z = 609$ stands for the molecular ion peak of complex (without water of crystallization). The proposed fragmentation pattern of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ is given in the Scheme 1. The measured molecular weights were consistent with expected values and the mass spectrum of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ complex is shown in Fig. 8.

3.5. Antimicrobial screening

The antibacterial activity of the standard drug (ciprofloxacin), ligand (L) and their metal complexes was screened against different bacterial strains as stated above. *S. aureus* is the preliminary screening test organism of choice for several reasons. Being a systemic pathogen with an ability to develop antibiotic resistance more readily than any other bacteria, the laboratory animals can be readily infected.

The inhibition of growth for these Gram-positive organisms produced by various concentrations of the test compounds was compared under identical conditions with the inhibition of growth for same organisms by ciprofloxacin (a standard antibiotic showing resistance to the growth of organism). Similarly, the inhibitions of the Gram-negative organism growth produced by the test compounds were compared with those for same concentrations of ciprofloxacin, which is a broad spectrum antibiotic. A standard volume (5 ml) of Luria broth medium (2%) to support the growth of the test organism was added to several labeled sterile stopper identical assay tubes. A solution of each test compound was prepared in DMSO and a series of dilutions was prepared. Concentrations tested were 0.25–20 ppm of the ligand and their metal complexes under investigation, a broad-spectrum antibiotic, the respective metal salt (20–800) ppm dissolved in DMSO and a blank (DMSO). A control tube containing no test compound was also included. A 0.1 ml aliquot of the test organism from the overnight grown test cultures was added. All these operations were carefully performed under aseptic conditions. Assay tubes were incubated at 30 °C for 24 h. The resultant turbidities were measured using a Systronics spectrophotometer model number 106. The minimum inhibitory concentration (MIC) of a test compound is the lowest concentration showing no visible turbidity. However, the final concentration of bacterial growth inhibition produced by a certain concentration of the test compound was calculated using the following relationship:

$$\% \text{inhibition} = [\text{Tc} - \text{Tt}/\text{Tc}] \times 100$$

where Tc is the turbidity of the control and Tt is the turbidity of the specific treatment or the test compound. The metal complexes exhibited strong activities against two Gram-negative (*E. coli*, *S. marcescens*) and two Gram-positive (*S. aureus*, *B. subtilis*) microorganisms (Parekh et al., 2005). The minimum

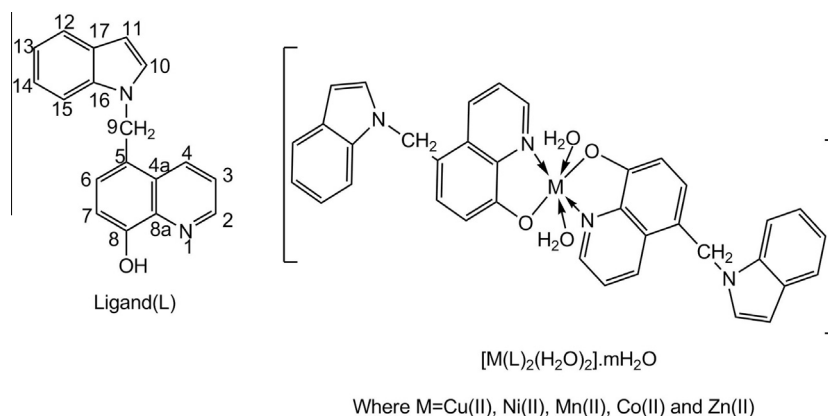


Figure 1 The structure of ligand and proposed structure of metal complexes.

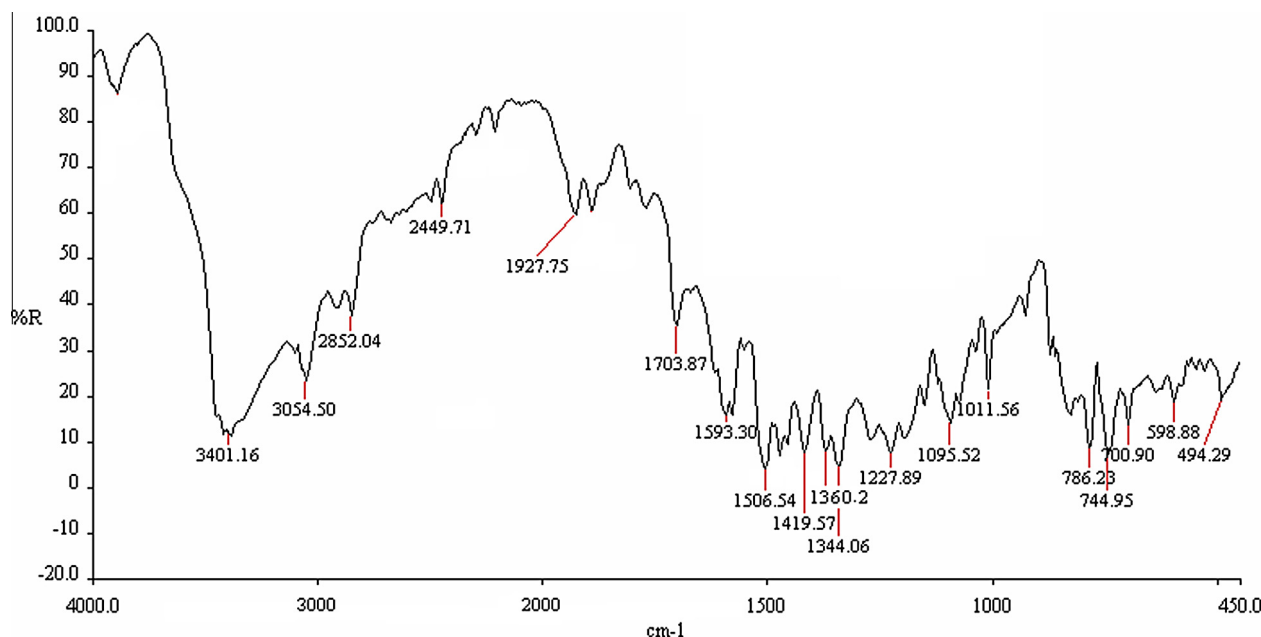


Figure 5 The FT-IR spectrum of ligand.

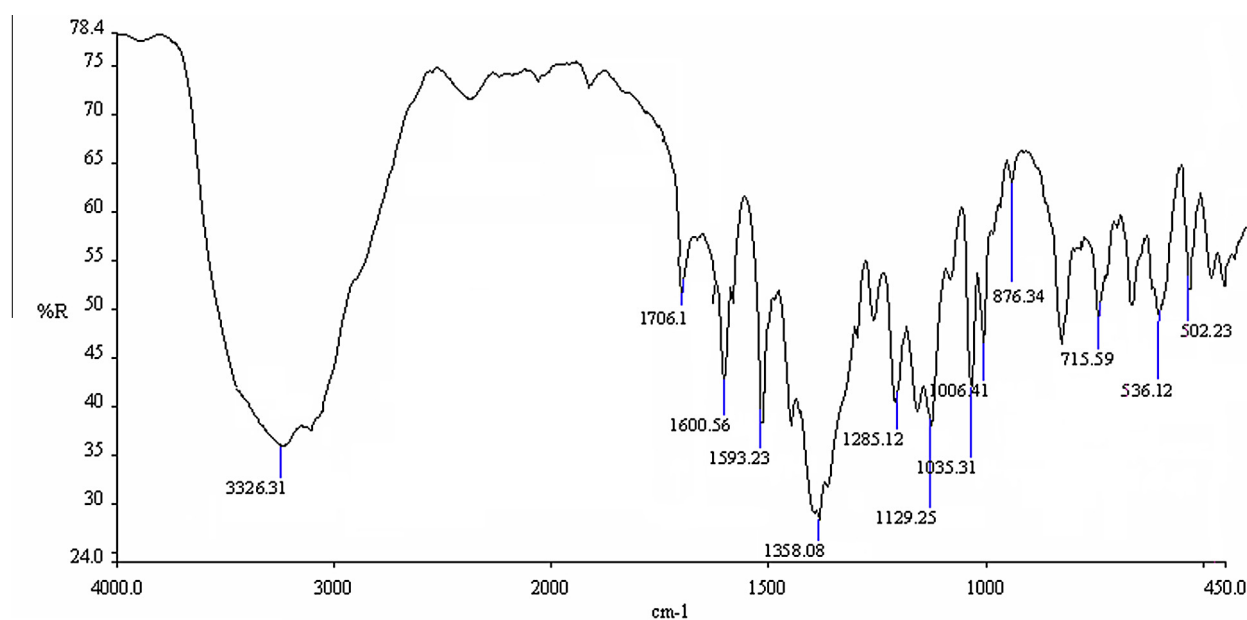


Figure 6 The FT-IR spectrum of $[Cu(L)_2(H_2O)_2]$ complex.

inhibitory concentration of antimicrobial activity data of the compounds is summarized in Table 5. A comparative analysis showed a higher antibacterial activity of the metal complexes than free ligands and metal salt. Some of the metal complexes exhibited moderate activities as compared with the standard drug ciprofloxacin. It was also observed that some of the metal complexes were more potent bactericides than the ligands. This enhancement in antibacterial activity is rationalized on the basis of Overtone's concept, Tweedy's chelation theory and the partial sharing of the positive charge of metal ions with donor groups (Talaviya and Chaudhari, 2013; Chohan et al., 2004). This may support the argument that some type of bimolecular

binding to the metal ions or intercalation or electrostatic interaction causes the inhibition of biological synthesis and prevents the organisms from reproducing. The results of our studies (Table 5) indicate that metal complexes have a good activity against ligand and all bacterial strains. The strong antimicrobial activities of these compounds against tested organisms suggest further investigation on these compounds.

4. Conclusion

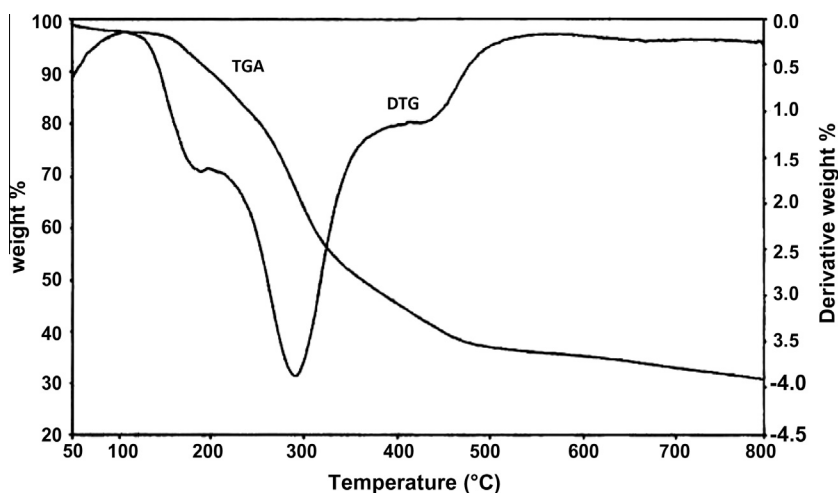
All the synthesized compounds were screened for their bioassay. The metal complexes exhibited strong activities against

Table 3 Thermoanalytical results (TG, DTG) of the metal complexes.

Compounds	TG range (°C)	DTG max (°C)	Mass loss (%) observed (calcd.)	Assignment
[Cu(L) ₂ (H ₂ O) ₂]	50–190	119	4.62 (4.67)	Loss of two coordinated water molecules
	190–455	–	40.04 (40.10)	Removal of some part of ligand
	455–80	648	47.19 (47.22)	Removal of remaining part of ligand leaving CuO residue
[Ni(L) ₂ (H ₂ O) ₂]	50–200	147	4.67 (4.70)	Loss of two coordinated water molecules
	200–440	289	39.68 (39.71)	Removal of some part of ligand
	440–800	–	48.13 (48.15)	Removal of remaining part of ligand leaving NiO residue
[Co(L) ₂ (H ₂ O) ₂]	50–210	121	4.67 (4.70)	Loss of two coordinated water molecules
	210–435	–	41.83 (41.90)	Removal of some part of ligand
	435–800	647	45.92 (45.94)	Removal of remaining part of ligand leaving CoO residue
[Mn(L) ₂ (H ₂ O) ₂]	50–185	165	4.71 (4.73)	Loss of two coordinated water molecules
	185–405	394	40.10 (40.17)	Removal of some part of ligand
	435–800	665	47.39 (47.41)	Removal of remaining part of ligand leaving MnO residue
[Zn(L) ₂ (H ₂ O) ₂]	50–205	152	4.62 (4.66)	Loss of two coordinated water molecules
	205–410	–	40.82 (40.90)	Removal of some part of ligand
	410–800	496	46.18 (46.20)	Removal of remaining part of ligand leaving ZnO residue

Table 4 Thermodynamic data of the thermal decomposition of metal complexes.

Compounds	TG range (°C)	E _a (kJ mol ⁻¹)	n	A(s ⁻¹)	S* (J K ⁻¹ mol ⁻¹)	H* (kJ mol ⁻¹)	G* (kJ mol ⁻¹)
[Cu(L) ₂ (H ₂ O) ₂]	50–190	11.45	0.99	9.47	–96.74	9.45	42.54
	190–455	13.30	1.00	1.60	–97.64	10.02	60.54
	455–80	14.21	0.99	0.86	–99.71	11.0	72.42
[Ni(L) ₂ (H ₂ O) ₂]	50–200	3.02	1.00	0.04	–102.34	–0.22	42.30
	200–440	10.16	1.00	0.20	–100.18	5.41	61.88
	440–800	30.57	0.98	19.55	–95.81	25.00	89.22
[Co(L) ₂ (H ₂ O) ₂]	50–210	3.28	0.98	0.23	–100.06	0.68	32.64
	210–435	14.61	0.99	1.06	–99.00	9.85	66.49
	435–800	27.55	1.00	2.22	–97.01	20.41	102.72
[Mn(L) ₂ (H ₂ O) ₂]	50–185	3.08	1.00	0.10	–101.41	0.35	32.49
	185–405	6.05	1.01	0.10	–100.40	2.33	57.51
	435–800	33.65	0.98	8.25	–96.20	26.85	106.00
[Zn(L) ₂ (H ₂ O) ₂]	50–205	3.11	1.00	0.14	–100.14	0.28	39.29
	205–410	6.07	0.99	0.22	–99.19	2.29	58.87
	410–800	33.66	0.98	5.25	–95.82	26.73	94.21

**Figure 7** TG/DTG curves of the [Cu(L)₂(H₂O)₂] complex.

two Gram-negative (*E. coli*, *S. marcescens*) and two Gram-positive (*S. aureus*, *B. subtilis*) microorganisms. In comparison with the ligand, the metal complexes were more active against one or more bacterial strains, introducing a novel class of metal-based bactericidal agents.

The information regarding the geometry of metal complexes was obtained from their electronic and magnetic moment values. From the overall information obtained, the metal complexes are supposed to be structurally arranged in tetragonally distorted octahedral geometry.

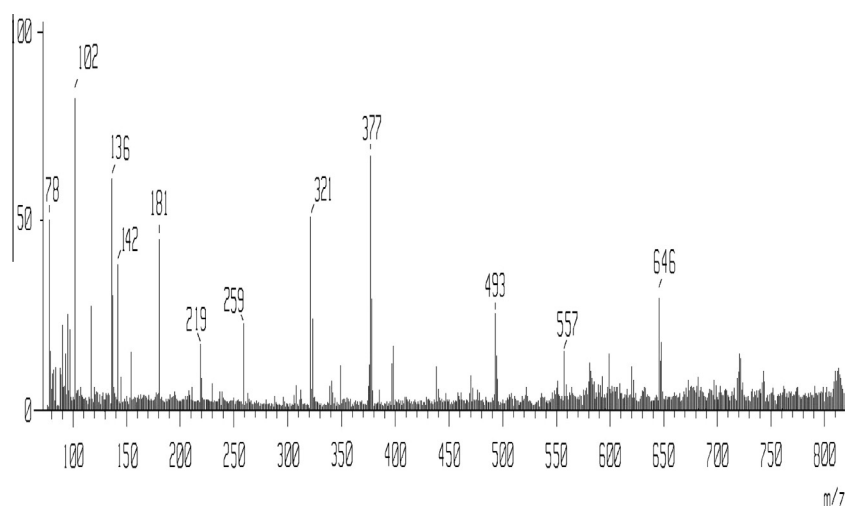


Figure 8 Mass spectrum of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ complex.

Table 5 Minimum inhibitory concentrations (in ppm) of the compounds against bacteria.

Compounds	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Serratia marcescens</i>
Ciprofloxacin	0.5	0.7	0.6	0.7
L	100	125	165	125
$[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$	1.25	1.00	0.25	1.00
$[\text{Ni}(\text{L})_2(\text{H}_2\text{O})_2]$	2.50	2.50	1.60	2.00
$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$	2.00	2.00	2.00	1.60
$[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$	2.50	5.00	2.50	2.00
$[\text{Zn}(\text{L})_2(\text{H}_2\text{O})_2]$	5.00	2.50	5.00	2.50
DMSO (Solvent)	—	—	—	—

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2013.07.056>.

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